Investigating the M^*He exciplexes, $M=\{$Li,Na,K,Rb,Cs,Fr$\}$: Density functional approach

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Potential curves for the ground and the first lowest excited states of the MHe (where $M=\{$Li,Na,K,Rb,Cs,Fr$\}$) exciplexes are calculated using the density functional theory (DFT) formalism. Relativistic calculations are carried out with and without spin-orbit (SO) coupling effect, using a zeroth order regular approximation (ZORA) approach. The depth D_e and position R_e parameters of the potential curves for the case without spin-orbit effect are presented and compared with other works. Potential curves for Li-He, Cs-He, and Fr-He without spin-orbit effect and Cs-He with the spin-orbit effect are shown. A bond analysis is presented too, since the central interest of the study of the exciplexes is the nature and the existence of the bonding states that are the origin of emission spectra observed experimentally for these systems. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1810133]

I. INTRODUCTION

Excited atoms often react to form bound electronically excited states of rather unexpected species (alkali–noble-gas combination) which are dissociative in the electronic ground state. These ''exciplexes'' molecules are often used as laser material since the ground state self-destructs by dissociation, and do not accumulate in sufficient amounts to reabsorb the laser light. Alkali-helium exciplexes are formed when one or more He atoms are attracted into the nodal plane of the excited p orbital of alkali atoms, the present study is done for a single He atom, in order to validate the ability of density functional theory (DFT) to describe this kind of interactions correctly in comparison to *ab initio* and semiempirical methods.[1–6] The formation of $M^*\mathrm{He}_n$ $(n=1,...,5)$ exciplexes have been proposed as the cause of the quenching of fluorescence emission.[7,8] In these exciplexes the crossing between the excited and the ground state potential energy surface opens the possibility of a decay via nonradiative transitions.[9] This does not apply to the heavier alkali (Rb, Cs,Fr), where the curve crossing mentioned above is not present due to the larger atomic cores and to the stronger spin-orbit coupling. In this case, the He atoms are not allowed to approach the waist of the p orbital as much as in the case of Li, Na, and K. Exciplexes are not formed when the p orbital is aligned perpendicularly to the helium surface (excitation), in this case the bare atom desorbs. Aligning the p orbital parallel causes mainly the formation of MHe $(M=\mathrm{Na,K})$ diatomic exciplexes. Several theoretical studies attempted to give a clear description of the formation of the exciplexes and their emission spectra, especially the bond formation is discussed. Thus computing the potential curves of the exciplexes, characterized by two parameters (depth D_e and position R_e), enables us to explain the experimental data. The best known model in this field is based on the semiempirical pair potential model given by Pascale.[2] He used l-dependent pseudopotentials defined from spectroscopical data to describe the e^--M^+ and e^--He interactions. Recently *ab initio* methods have been used. Enomoto *et al.*[1] carried out calculations of adiabatic potential curves of M^*He within the restricted Hartree-Fock formalism. Kunz[3] performed a configuration interaction calculations for the Cs-He system based on restricted open shell Hartree-Fock orbitals of Cs, obtained from a spin-averaged relativistic calculation using the Douglas-Kroll-transformed spin-free no-pair Hamiltonian. Interatomic potentials are of fundamental importance in many physical processes since they determine the sizes of collision cross sections, relaxation, and reaction rates as well as the widths and shapes of the spectral lines. Calculation of these potentials are notoriously difficult and experimental verification not easier to obtain. For all the theoretical methods mentioned above, most of them include adjustable model potentials to yield more realistic results. In this paper we propose to use density functional theory to compute the potential energy curves of alkali–rare-gas systems, which means a genuine first-principles method. It is known that DFT is basically a ground-state theory and it handles not in a good way the weak long-range terms involved in van der Waals interactions. But there are three reasons behind the choice of DFT:

(1) Diatomic exciplexes with different symmetries of states are studied.

(2) Alkali atoms and helium atom repel each other by virtue of Pauli principle. However, alkali atoms excited to the lowest lying P states can exert attractive potential on helium atom and lead to bound states (M^*He). In our study, only the first lowest excited states are investigated.

(3) The obtained results are in a good agreement with the available experimental data and also with the other cited methods.

We used the relativistic zeroth order regular approximation[10,11] (ZORA) Hamiltonian, which is of zeroth

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TABLE I. Depth (D_e in cm^{-1}) and position in (R_e in angstrom) of the $A\,^2\Pi$ potential wells of the M^*He systems.

	Present work		a		b		c		d		e	
	D_e	R_e	D_e	R_e	D_e	R_e	D_e	R_e	D_e	R_e	D_e	R_e
Li	1240	1.82	1025	1.82	500	1.85			850	1.85	850±100	1.83±0.4
Na	730	2.3	511	2.3	210	2.4	299	2.42	427	2.26	480± 50	2.33±0.1
K	480	2.8	245	2.8			190	2.8				
Rb	276	3.22	134	3.3								
Cs	230	3.38	112	3.49								
Fr	186	3.57										

[a]Model potential calculations of Pascale (Ref. 2).
[b]*Ab initio* self-consisted-field results calculations of Krauss (Ref. 26).
[c]Model potential calculations of Hanssen (Ref. 27) for NaHe and of Masnou-Seeuws (Refs. 28 and 4) for KHe.
[d]Model potential calculations of Roberts (unpublished) for LiHe (taken from Ref. 9) and of Peach (unpublished) for NaHe (taken from Ref. 20).
[e]Experimental results of Havey (Ref. 9) for LiHe and NaHe.

order in the perturbation expansion of $E/(2mc^2-V)$. The approach is variationally stable and there is no need for renormalization. The spin-orbit operator is regularized and the scalar relativistic corrections are good. In the following section, we present the computational details of the method used. In the third section the result of the calculations is presented. We calculated potential curves for the electronic lowest two states, the excited $\tilde{A}$ state and the ground $\tilde{X}$ state of M^*He with and without spin-orbit coupling. We display the depth D_e and position R_e for MHe, where $M=\{$Li,Na,K,Rb,Cs,Fr$\}$. Results without spin-orbit coupling are shown for the sake of comparison with other works. Potential curves of Li-He, Cs-He, and Fr-He without spin-orbit effect and potential curve for Cs-He with spin-orbit coupling are presented. A tool, which is bond analysis, for the treatment of the exciplexes systems is also discussed.

II. COMPUTATIONAL DETAILS

We carried out a relativistic density functional calculations of potential energy curves of MHe systems within the ZORA (Refs. 10 and 11) formalism with and without spin-orbit coupling using the Amsterdam density functional (ADF) package,[12,13] version (2003.01). Both the local density approximation (LDA) and the generalized gradient approximation (GGA) for exchange-correlation functionals were used. The LDA was applied with the Vosko, Wilk, and Nusair functional.[14] The GGA was applied by using the Perdew-Wang (PW91) functional.[15] All the other available functionals were tested, and the cited functional yields to the most accurate results. The frozen-core approximation for the inner-core electrons was used. The orbitals up to $5d$ for francium (Fr), $4d$ for cesium (Cs), $4p$ for rubidium (Rb), $3p$ for potassium (K), $2p$ for sodium (Na), and $1s$ for lithium (Li) were kept frozen. The valence shells were described by a high diffuse basis, ZORA triple-ζ slater-type orbitals (STO) set plus two polarization functions (ZORA/TZ2P),[16] the choice of this basis set is based on the role of the polarization of the He and the alkali atoms. The accuracy of the results is influenced by type of the numerical grid,[17] since integrals in ADF are evaluated by numerical quadrature.[18] We found that for the relativistic studies of weak interactions very fine numerical grids are needed; by very fine we mean high numerical integration grid.

III. RESULTS AND DISCUSSION

A. Potential curves without spin-orbit coupling

In order to obtain experimental potential curves of systems dominated by weak interactions, semiempirical and empirical potential[2,19,3,20] models are used extensively to accomplish this task especially for the exciplexes. Our DFT results are in good agreement with these models, Table I shows the potential curve parameters D_e and R_e for a set of alkali He. The complete set, namely, Li, Na, K, Rb, Cs, and Fr is listed. Our results show that there is a very good agreement for the position R_e of the potential well when compared with the other works, and especially with Pasclale's model.[2] For the depth parameter D_e, there is a slight overestimation in comparison to the other works. This is expected since DFT, especially LDA, is frequently overbinded and there are no adjustable parameters used in it. Our results, in which we introduce a different system, the Francium-Helium exciplexes, confirm as well as the other methods that R_e increases and D_e decreases with the increase of the size of the alkali atoms, i.e., in this order Li→Fr.

Figure 1 represents the potential curves of Li-He, and Fig. 2 represents the potential curves of Cs-He and Fr-He without spin-orbit interaction. In both figures the $A\,^2\Pi$ and $X\,^2\Sigma$ states are represented. The potential curve for the $A\,^2\Pi$ state is attractive, and the potential well becomes deeper for the Li (the lightest alkali atom). The potential curve for the $X\,^2\Sigma$ state is almost repulsive. In this case we did not take into account the fine-structure splitting of the exciplexes, since the fine structure splitting of Li for the first p state is negligible [0.3 cm^{-1} for Li (Ref. 21]. However, the strength of the spin-orbit coupling is much bigger for the heavier alkali-metal atoms. For example, the fine structure of the p orbitals is experimentally 554 cm^{-1} for Cs (Ref. 22), whereas our calculation predicts 572 cm^{-1}. In the following section, we will take this effect into account, and the poten-

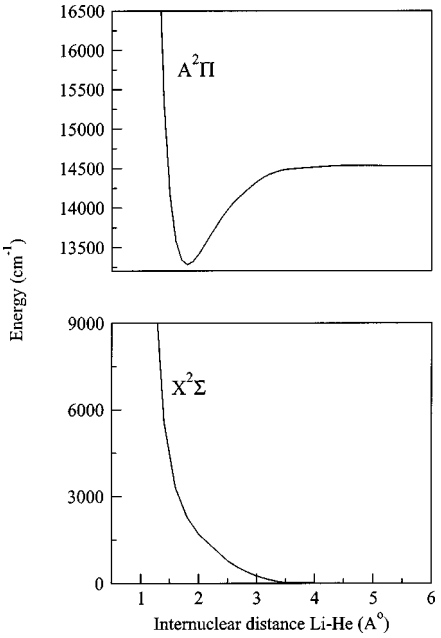

FIG. 1. Potential curves for the $A\,^2\Pi$ and $X\,^2\Sigma$ states of Li-He obtained with ZORA-DFT calculations.

tial curve of CsHe including spin-orbit effect will be presented.

B. The effect of the spin-orbit coupling, case of Cs-He

The configurations of the valence shells of all alkali atoms are the same, ns^1 with $n=2$ for Li, $n=3$ for Na, $n=4$ for K, $n=5$ for Rb, $n=6$ for Cs, and $n=7$ for Fr. The lowest excitation promotes an ns electron to np orbital. The

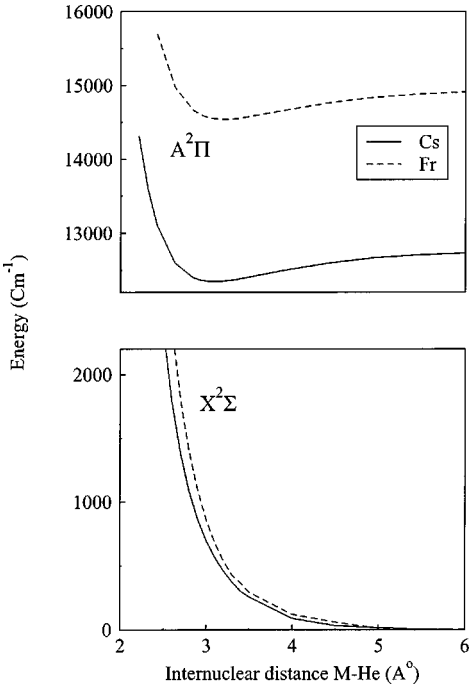

FIG. 2. Potential curves for the $A\,^2\Pi$ and $X\,^2\Sigma$ states of Cs-He and Fr-He obtained with ZORA-DFT calculations.

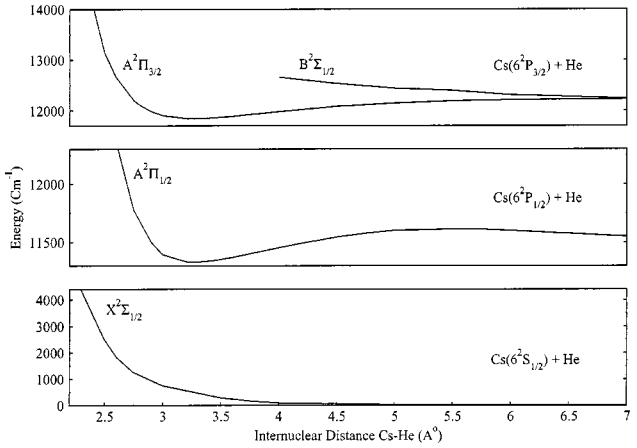

FIG. 3. Cs-He potential curves including the spin-orbit interaction. The electronic state of the separated atomic pair is also shown.

spin-orbit coupling becomes increasingly more important as the atomic number of alkali atoms increases. Since most of the spin-orbit effects are due to incomplete shielding by the core electrons whereas most of the chemical forces between atoms are due to the valence electrons, a significant simplification of the problem should be possible in which these two effects are considered separately. This separation has been utilized in the present work by first determining potential curves (the preceding section) neglecting the spin-orbit effect in the ZORA Hamiltonian, and then calculating potential curve including this effect.

Figure 3 represents the ground and excited states potential curves of CsHe exciplexes with spin-orbit coupling, the labels used are the dominant $|LSL_zS_z\rangle$ componant at small R. The lower potential curve is for the $X\,^2\Sigma_{1/2}$ state which corresponds to $\mathrm{Cs}(6\,^2S_{1/2})+\mathrm{He}$. This potential curve is repulsive. The potential curve with the highest energy among the three excited states is for $B\,^2\Sigma_{1/2}$ state corresponding to $\mathrm{Cs}(6\,^2P_{3/2})+\mathrm{He}$. This potential curve is also repulsive, so it does not exibit a well to make a bound. The $A\,^2\Pi_{1/2}$ state corresponding to $\mathrm{Cs}(6\,^2P_{1/2})+\mathrm{He}$ has a well predicted at about 3.4 Å by our calculations (3.5 Å from Refs. 1 and 2) deep enough to form a bond or a quasibond. This potential has also a barrier at 5 Å which is in very good agreement with the data of Ref. 1. The $A\,^2\Pi_{3/2}$ state corresponding to $\mathrm{Cs}(6\,^2P_{3/2})+\mathrm{He}$ has a potential curve with a well at $R=3.4$ Å, and there is no barrier in this case. Enomoto *et al.*[1] obtained the same result.

The fact that the bonding or quasibonding state $A\,^2\Pi_{3/2}$ has no barrier and that the $A\,^2\Pi_{1/2}$ state has a barrier shows that this last state is the more stable one; hence an emission spectra can be observed from this state. Our next work will address this point and will treat the theoretical prediction of emission spectra of exciplexes using DFT. Another interesting point to analyze from these results is the clear avoided crossing of states with the same spin symmetry. Thus, DFT clearly predict excited states as well as the post-Hartree-Fock methods.

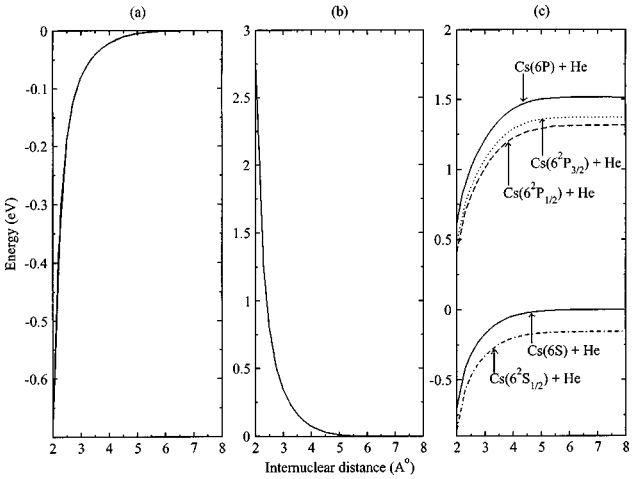

FIG. 4. Bond analyses of Cs-He with spin-orbit effect (dashed and dotted lines) and without spin-orbit effect (solid lines). (a), (b), and (c) indicate, respectively, the electrostatic interaction, the Pauli repulsion, and the orbital interaction.

C. Bond analysis

In the program[12,13] we used, there is a three-step procedure to build the chemical bond[23–25] MHe. In fact the approach is based on fragments. This applies not only in the analysis at the end of computation but also in the setup of the calculation. The computation of the molecule from its constituent fragments takes place in three steps, and these are reflected in the analysis of bond energy components. These three steps yield the three following interactions: *electrostatic interaction*, *Pauli repulsion*, and *orbital interaction*. Thus, we consider a chemical bond as a sum of three contributions: classical electrostatic forces (ΔE_{el}), covalent bonding (resonance of the wave function) (ΔE_{orb}), and the Pauli (exchange) repulsion (ΔE_{xc}). Figure 4 represents the bond analysis of the Cs-He system with and without spin-orbit coupling. We can see that the only part that contributes significantly to the chemical bond of exciplexes is the orbital interaction part. Thus for both the ground and excited states, the electrostatic interaction and Pauli repulsion are the same, which means that the resonance of the wave function of excited p orbitals of Cs (and the other alkali as well) makes an attractive interaction with He for $R=R_e$. The electrostatic contribution is attractive and it is compensated by the Pauli replusion.

IV. CONCLUSION

Both DFT and *ab initio* methods are nonparametric, i.e., applicable to any molecule. In this paper we showed that DFT is able to provide an accurate description of a different type of systems: the exciplexes. Hence, we can conclude that we got the potential curves parameters R_e and D_e, and the expected spin-orbit effect (Fig. 3) is in good agreement with the standard models. Also our calculated fine structure splitting for free atomic excited Cs (572 $\mathrm{C\,m^{-1}}$) is in very good agreement with the experimental one (554 $\mathrm{C\,m^{-1}}$), we can conclude that DFT is simple and suitable method to treat exciplexes.

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